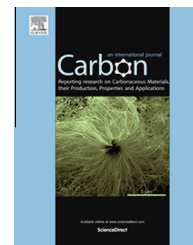


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Elemental analysis of nanodiamonds by inductively-coupled plasma atomic emission spectroscopy

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ABSTRACT

A 68-element survey study was carried out on micro-impurities from 20 commercial nanodiamond samples from eight international manufacturers. The measurements were made using inductively coupled plasma atomic emission spectroscopy with detection limits for most elements below 1 ppm. Various methods of sample preparation were compared: direct introduction of suspensions, ashing with microwave-assisted acid digestion, and microwave-assisted acid extraction, and their advantages and disadvantages evaluated. The work demonstrates the feasibility of nanodiamond analysis by direct slurry nebulization, which provides a multi-element, rapid, simple, and relatively low-cost route for nanodiamond purity estimation. Most of the samples contain relatively high amounts of Fe, Na, Ca, Si, Cu, Al, S, and Ti (>100 ppm), while Pb, Zn, K, Mn, B, Cr, Mg, Mo, Sn, W, Ba, Sb, Co, and Sr are at low but significant amounts. In addition, in several samples, we found some uncommon elements like Ag, Ce, Y, Hf, Zr, and Hg. This study provides new possibilities for certifying nanodiamond purity, understanding their properties and behavior, and advancing their production technology.

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1. Introduction

Detonation nanodiamonds (NDs) gain much attention for biomedical and clinical applications [1] and high-technology purposes [2–7] due to their unique properties. NDs are technological products that contain not the diamond substance only, but also various kinds of accompanying substances. These substances vary in nature and are present in relatively large amounts. They are formed either during the detonation synthesis itself or in subsequent processing of the diamond mixture. They can be divided into several groups [8–11]: (1) impurities in the crystal lattice of the diamond

nuclei (N, B atoms, sometimes metals); (2) chemically bonded with the surface layer of diamond nuclei (usually, various functional groups such as COO, COOH, OH, NH, etc.); (3) physically adsorbed (metal microparticulates and nonmetallic oxides, carbides, and insoluble salts); and (4) chemically adsorbed (gases, metal cations, anions of acids). From the viewpoint of the elemental composition (in a wide sense) NDs consist of C, H, O, N (90–99% total), and metal and some nonmetal atoms (the unburnt residue). Such impurities appear due to the interaction of the explosion wave with the reaction chamber walls (Fe, Cr), instrumentation corrosion during the purification (Cr, Ti) [11], from explosion initiators

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(Cu, Pb, Hg) [8], and adsorbed by already formed nanodiamonds [7,12] from water during their separation from the separation-chamber charge and purification (Si, Ca, Fe) [11].

Many ND properties that are relevant for their application (aggregate size, surface groups, optical and colloidal properties, etc.) depend on their production and purification technology. In particular, very relevant is the ND elemental composition—and primarily the content of metals and impurity nonmetals—because they may be hazardous even at their trace quantities. It is even more important if we deal with nanomaterials for biomedical applications [1] or catalysis [2,3,13], where the purity control is crucial. Such metals like Cu, Cr, Ni, Zn, Cd, Hg, Ag and other as well as some nonmetals like As maybe toxic, especially in their nanoparticles. This is confirmed by a number of studies e.g. for Cu [14], Ag [15], Zn [16,17], Ti [18] etc. In the case of NDs, these metals can exist at the particle surface and thus, manifest their toxicity.

These is not obvious however, that such toxicity, observed for purely metal clusters will be typical of atoms of metals at the surface. This was confirmed by several latest studies on various types of toxicity of nanoparticles, including carbon nanomaterials, especially nanotubes [19–22] due to their increasing use in medicine and related areas. It was found that among the factors, affecting the risk assessment of these materials, metal impurities play an important part [20,21].

Concerning NDs, *in vivo* studies with mice [23–26] revealed that NDs accumulate in liver, lungs, bones, spleen and heart and then are slowly removed from the body. Their toxic effect on these organs is ambiguous. However, taking into account the toxicity of metal nanoparticles the problem of investigation of metal impurities in NDs seems topical.

Recent studies showed that complexes of NDs with some metals show significant catalytic activity, in particular Pt (5–15% w/w) [27]; Pd (3–15% w/w [27,28]; 0.5–5% [29]); Au (2% w/w) [29]; Ni (7% w/w) [30,31]; Fe (6–7% w/w) [32,33]. In these papers, the amounts of metals were specially introduced, and their concentrations in the resulted compositions were determined by electron probe X-ray microanalysis [27,28] or atomic-absorption spectroscopy [29,33]. The catalytic activity strongly depends on the composition of the nanodiamond-metal material [30], and the most important is the fact of formation of metal particles at ND surface [29]. Furthermore, elemental impurities change such ND properties like thermal and oxidative resistance [34,35].

Until now, not much attention was focused on multielement chemical analysis of NDs, although its importance was declared from the very start of ND research. Probably, this situation is due to a need to strictly monitor the purity of the preparation, while ND traceability is still not achieved [36]. Hence, and the available data on ND elemental composition are fragmentary and incomplete (and treated by the authors as auxiliary). Usually, the estimation of the sample purity is limited to the measurement of the mass of the unburnt residue only [11,37–41] or the total content of metal impurities [34,39]. Nevertheless, total parameters, though useful, do not provide a clear picture of the purity. As a whole, this may form a vicious circle: as long as there is no control of trace elements in NDs, there are no new ND applications and vice versa. The situation is gradually changing today. Relatively scarce investigations on the particular microimpurity

compositions of nanodiamonds showed that metal impurities consist of Fe, Cr, Ni, Al, Na, K, Ca, Ti, Pb, etc., nonmetals are Si and B [10,41–43], sometimes Cl and S are detected [44]. Some authors declare that some elements (Fe and Cu) cannot be fully removed from nanodiamonds [9,11,38]. To sum up, a systematic ND impurity study has not been conducted yet, while the elemental composition of NDs should be known very reliably and precisely.

The development of a reliable analytical tool is the obvious first step to render ND properties traceable and to improve and advance the production technology. Firstly, a method for the analysis of microimpurities in NDs should meet several requirements: it should be multielement and rather precise and sensitive; a rather simple sample preparation and high rapidity are desirable. Methods of atomic spectroscopy meet these requirements, and, thus, they were used toward this aim. In particular, the impurity elements were determined in NDs by atomic emission spectroscopy [9], arc atomic emission spectroscopy [38], energy-dispersive X-ray spectroscopy [42,45], secondary-ion mass spectrometry [44], electron probe microanalysis [11,34], and X-ray photoelectron spectroscopy [43]. Metal impurities were quantified by the measurements of magnetic susceptibility of samples [46]. Electron-spin resonance spectroscopy was used for the detection of Fe^{3+} , Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and semiquantitative determination of differences in the impurity concentrations depending on the synthesis method and subsequent treatment [47,48]. Quite recently, Nesterenko and his co-authors have presented a rather deep study of elemental composition of NDs using inductively-coupled plasma mass-spectrometry [49]. However, this paper deals with the analysis of only few types of nanodiamonds produced worldwide and did not cover all the aspects of the elemental composition of such complex objects of nanodiamonds that require not only the analysis but also sample preparation techniques and error management, i.e. the development of a reliable analytical tool.

Secondly, from the viewpoint of a reliable tool for materials characterization, the analysis of each material should be preceded by the investigations of the applicability of the method in question to this material with an estimation of the main error sources. To-day, we did not find such investigation related to nanodiamonds.

Thirdly, this method should provide a combination with various sample-preparation techniques that provide bias-free, simple, and traceable delivery of samples to the analytical instruments, including flow and online control (for biomedical applications). Thus, the development of an analytical tool should take it into account.

Thus, there is still a need for a traceable and reliable analytical tool for ND impurity characterization. In our opinion, this problem can be solved using the state-of-the-art method of atomic spectroscopy—atomic-emission analysis with inductively coupled plasma (ICP–AES). This method is *de facto* standard for various environmental, high-technology, clinical, and pharmaceutical analysis. In this paper, we discuss the analytical possibilities of ICP–AES for accurate and precise multielement quantification of NDs with various sample-preparation strategies. We compared three types of ND preparation for quantitative ICP–AES measurements: (1) preparation of aqueous dispersions (slurries) for direct introduction

into the spectrometer; (2) ashing samples and acid digestion of ash in a microwave oven; (3) nitric acid treatment of samples in a microwave oven (acid extraction). Though we are not going to compare the existing ND materials in terms of quality, we attempted to gather a most representative collection of existing samples of NDs, which are most frequently used in the basic and applied studies.

2. Experimental

2.1. Nanodiamond samples

Commercially available NDs were used throughout; product names and manufacturers are listed in [Table 1](#).

2.2. Equipment

An axial ICP–AES 720-ES spectrometer (Agilent Technologies, USA) was used for measurements with a low flow axial quartz torch with 2.4 mm inner diameter injector tube (Glass Expansion, Australia), a double-pass glass cyclonic spray chamber (Agilent Technologies), a Seaspray concentric glass nebulizer (Glass Expansion), and a Trident Internal Standard Kit (Glass Expansion). For sample introduction, a SPS3 autosampler was used, some non-stable ND suspensions and solutions with precipitates were manually shaken directly before the analysis. A peristaltic pump used the white/white poly-vinyl chloride pump tube for feeding and the blue/blue one for drain. A La solution (50 ppm) internal standard was added on-line (orange/blue poly-vinyl chloride pump tube) to increase the accuracy of measurements. Conditions of ICP–AES measurements are presented in [Table 2](#). Total time for the measurement of a single sample was 2 min 35 s. The total required volume was 7 ml. Results were collected and processed by ICP Expert software 2.0.5 (Agilent Technologies).

Atomic emission lines are presented in [Table 3](#). All lines were measured simultaneously (a MultiCal mode). Linear and rational (quadratic) functions were used for the calibration. The position and baseline correction were made for all the peaks of uncommon elements using the tools of the spectrometer software.

2.3. Other equipment

A Multiwave 3000 microwave oven (Anton Paar, Austria) with an XF 100 rotor was used for the acidic digestion of ND ash and acid treatment of ND samples. A Kern 770 analytical balance (Germany) was used for dry powder samples weighting. A HG63 Moisture Analyzer (Mettler–Toledo AG Laboratory & Weighing Technologies, Switzerland) was used for water content determination. Automatic “weight loss per unit of time” switch-off criterion was used for measurements, when drying is automatically ended when the mean weight loss (Δg in mg) per unit of time (Δt in seconds) drops below a preset value. A SNOL 20/300 heating oven (Snol-Term Ltd., Russia) was used for the evaporation of ND aqueous dispersions. A SNOL 6.7/1100 muffle furnace (SNOL Ltd., Lithuania) was used for ashing ND samples in a platinum crucible. A GRAD 28-35 ultrasound bath (USB) from Grad-Technology (Russia) was used

for preparing ND dispersions in water. Automatic Eppendorf Research pipettes (Eppendorf International, Germany) were used for the preparation of calibration solutions. Polypropylene volumetric flasks (Vitalab, Germany) and polypropylene test tubes (Axygen, USA) were used for solution preparation and storage.

2.4. Other reagents

Deionized water ($18.2 \text{ M}\Omega \times \text{cm}$ from a Milli-Q Academic system, Millipore, France) was used for the preparation of all the solutions and washing. 69%-Nitric, 37%-hydrochloric (PA-ACS-ISO grade, Panreac, Spain), and 40%-hydrofluoric (puriss. p.a., ISO grade, Sigma-Aldrich) acids were used for ND ash digestion and acidic extraction. An ICP–MS 68 element standard solution, 100 ppm (High Purity Standards) was used for calibration (10–2000 ppb). For elements at their high concentrations (Ti, Fe, P, Na, Ca, K, Mg, and Zr), additional mixed calibration solutions (separately prepared by mixing individual standard solutions from High Purity Standards) were used. An internal standard solution of La (50 mg/L) was prepared from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

2.5. Procedures

The measurement results are presented in accordance with the requirements of ISO/IEC 17025:2005 [50].

2.5.1. Technique 1 of solution preparation

ND powders ($500.0 \pm 0.1 \text{ mg}$) were placed into polypropylene test tubes; next, (50.00 ± 0.12) ml of deionized water was added to all the test tubes and mixed. Next, a suspension was treated in the USB for 5–6 h.

2.5.2. Technique 2 of ashing and digestion

ND powder ($250.0 \pm 0.1 \text{ mg}$) was placed into an opened platinum crucible, transferred into a heating oven at a necessary temperature (see below), and kept for 2–3 h until total ashing. Next, a crucible was cooled in air at room temperature, 1 ml of HNO_3 was added, and the suspension was quantitatively transferred into XF100 Teflon vessels for microwave digestion. A crucible was triply washed with 1 ml of HNO_3 , the acid with ash residues was also placed into the vessel with the main part of the residue. Next, 2 ml of HCl were added into the vessel, it was closed and put into the microwave oven under conditions presented in [Table 4](#). After process finishes, suspensions were transferred into polypropylene (25.0 ± 0.1) ml volumetric flasks, cooled at room temperature, and diluted with deionized water. Solutions were stored in 50 ml polypropylene test tubes. Temperatures for ashing: RUDDM 2011 and 2012, SDND—550–600 °C, but not higher, RDDM—850–900 °C, all other—650 °C.

2.5.3. Technique 3 of acid extraction

ND powders ($250.0 \pm 0.1 \text{ mg}$) were placed into XF100 Teflon vessels for microwave digestion, 6 ml HNO_3 were added, and the vessels are manually shaken. Next, vessels were closed and put into the microwave oven under the conditions presented in [Table 4](#). After the process finish, suspensions

Table 1 – Nanodiamonds used in the survey.

Product name	Description	Manufacturer
RDDM	Modified nanodiamond material of RDDM grade, fraction 0–0.125	“Real-Dzerzhinsk” Ltd., Dzerzhinsk, Russia
RUDDM 2011 ^a	Modified nanodiamond material of RUDDM grade, fraction 0–150	
RUDDM 2012 ^a		
RUDDM non-fractionated	Modified nanodiamond material of RUDDM grade, non-fractionated	PlasmaChem GmbH, Germany
SDND	Single-Digit NanoDiamonds	
G	Nanodiamonds powder grade G	
G01	Nanodiamonds powder grade G01 (NanoPure-G01)	
G02	Nanodiamonds powder grade G02	
G01P	Nanodiamonds positively charged	
NanoAmando	NanoAmando	NanoCarbon Research Institute Co., Ltd., Japan Special Construction-Technological Bureau “Tekhnolog”, St. Petersburg, Russia
DNA-TAN	DNA-TAN	
DNA-STP	DNA-STP	
UDAG-S	UDAG-S, diamond-carbon powder	The Laboratory of ultradispersed diamonds of Joint Stock Company Federal Research and Production Center ALTAI, Biysk, Russia
UDA-S	UDA-S, ultradispersed diamond powder	JSC “SINTA”, Minsk, Republic of Belarus
UDA-S-GO	UDA-S-GO, ultradispersed diamond powder of deep purification	
UDA-SP	UDA-SP, ultradispersed diamonds	
UDA-GO-SP	UDA-GO-SP, deep purified ultradispersed diamonds	
UDA-GO-SP-M1	UDA-GO-SP-M1, modified ultradispersed diamonds, type M1	
UDA-GO-SP-M2	UDA-GO-SP-M2, modified ultradispersed diamonds, type M2	
UDD-NanoGroup	UDD, Ultra Dispersed Diamond	“NanoGroup Co.” Prague, Czech Republic “ALIT”, Kiev, Ukraine
UDD-Alit	UDD, Ultra dispersed diamond powder	

^a Different lots of the same ND product name purchased at different times.

Table 2 – Conditions of ICP–AES measurements.

Conditions for all lines registrations	
RF power (kW)	1.30
Plasma flow (L/min)	16.5
Axial flow (L/min)	1.50
Nebulizer flow (L/min)	1.06
Replicate read time (s)	30
Plasma stabilization delay (s)	10
Replicates	3
<i>Sample introduction settings</i>	
Sample uptake delay (s)	25
Pump rate (rpm)	15

were transferred into 25 ml volumetric flasks, cooled at room temperature, and diluted with water. Next, the suspension coagulated, the supernatant was separated from sediments and transferred to polypropylene test tubes.

2.5.4. Technique 4 of moisture measurements

Moisture contents in all commercial ND were determined by the thermogravimetry moisture analyzer. For this, a part of

each sample (1 g) was placed into the analyzer, heated to 105 °C and kept to a constant mass. The most precise automatic switch-off criterion (a fixed weight loss of 1 mg per 140 s) was selected.

3. Results and discussion

3.1. Sample preparation

NDs are rather complex objects for elemental analysis. On one hand, they contain 95–98% of the main element, carbon. Hence, all other elements would be at least at ppm levels. On the other hand, the elaborate technology of ND production and the previous results show that a wide range of elements can be revealed. At present, we do not know what impurities can significantly affect the course of certain experiments. Thus, we have to know the composition of ND materials to our best. This means that the selected analytical procedure must be multielement, sensitive, rapid, and desirably simple. ICP–AES procedures meet all these requirements. Unfortunately, like almost all the methods of analysis, ICP–AES needs an adequate calibration and a reliable standard reference material, and there are no such features for NDs now.

Table 3 – Emission lines used for ICP–AES analysis.

Elem.	Emission lines (nm)	Elem.	Emission lines (nm)
Ag	328.068, 338.289	Nd	401.224, 410.945, 430.357
Al	308.215, 394.401, 396.152	Ni	230.299, 231.604
As	188.98, 193.696, 197.198	Os	225.585, 228.228, 233.68, 236.735
Au	208.207, 211.068, 242.794, 267.594	P	177.434, 213.618, 214.914, 253.561
B	208.956, 249.678, 233.527	Pb	220.353, 261.417
Ba	233.527, 455.403, 493.408	Pd	340.458, 342.122, 351.694, 360.955
Be	234.861, 313.107	Pr	410.072, 422.293, 422.532
Bi	222.821, 223.061, 289.799, 306.771	Pt	214.424, 265.945, 273.396, 299.796, 306.471
Ca	393.366, 396.847, 422.673	Rb	420.179, 780.026
Cd	214.439, 226.502	Re	197.248, 221.427, 227.525, 346.045
Ce	418.659, 446.021, 456.236, 462.816	Rh	343.488, 350.252, 352.803, 369.236
Co	231.16, 237.863, 238.892	Ru	240.272, 245.657, 267.876, 349.894
Cr	267.716, 283.563, 313.205, 357.868	S	180.669, 181.972, 182.562
Cs	455.522, 697.327	Sb	217.582, 231.146
Cu	324.754, 327.395	Sc	335.372, 357.253, 361.383, 424.682
Dy	340.78, 352.398, 353.171, 387.211, 394.468, 400.045	Se	196.026, 203.985, 206.279
Er	326.478, 337.275, 349.91, 369.265, 390.631	Si	250.69, 251.432, 251.611
Eu	397.197, 412.972, 420.504, 443.558	Sm	359.259, 442.434, 446.734
Fe	238.204, 239.563, 259.94	Sn	189.925, 326.233
Ga	287.423, 294.363, 417.204	Sr	346.445, 407.771, 421.552
Gd	335.048, 336.224, 342.246, 358.496, 376.84, 379.638	Ta	238.706, 263.558, 267.59, 268.517
Ge	219.871, 259.253, 265.117	Tb	332.44, 350.914, 360.044, 367.636
Hf	263.872, 277.336, 301.29, 339.979	Te	214.282, 225.903, 238.579
Hg	194.164, 253.652	Th	283.73, 318.019, 335.123, 401.913
Ho	339.895, 341.644, 345.6, 379.675	Ti	334.188, 334.941, 336.122, 337.28
In	230.606, 325.609, 410.176	Tl	190.794, 351.923
Ir	212.681, 224.268, 236.804	Tm	313.125, 342.508, 379.576, 384.802
K	766.491, 769.897	U	367.007, 409.013
Li	610.365, 670.783	V	289.265, 292.401, 311.837
Lu	261.541, 307.76, 547.668	W	207.912, 220.449, 224.876, 248.923
Mg	279.553, 279.8, 280.27, 285.213	Y	360.074, 371.029, 377.433, 437.494
Mn	257.61, 293.305, 293.931	Yb	289.138, 328.937, 369.419, 398.799
Mo	281.615, 284.824, 289.099, 379.825	Zn	206.2, 213.857
Na	568.821, 588.995, 589.592	Zr	327.307, 339.198, 343.823, 349.619
Nb	313.078, 316.34, 322.547	La	333.749, 408.671, 492.178, 379.477, 379.082

* Some lines were not used for quantitative analysis due to spectral interferences, see the Section 3.

Table 4 – Conditions of microwave ash digestion and acid extraction.

Parameter	Value
Power	1000 W
Control parameter	Pressure (p-program)
Pressure limit	60 bar
Pressure rate	0.5 bar/s
Temperature limit	180–200 °C
Ramp	5 min
Hold	90 min ^a
Cooling	At 50 °C temperature
^a 60 or 180 min for acid extraction.	

Moreover, ICP–AES requires the sample introduction in a liquid phase. For this reason, we compared some approaches: the direct way of analysis using a slurry nebulization technique, classical ashing with digestion, and the acid extraction of impurities in microwave high-pressure vessels.

The main problem for direct elemental analysis of NDs lies in their insoluble nature. However, we found that NDs could be divided into two large groups. The first ND group spontaneously forms a finely dispersed colloid solution (SDND, RUDDM, and RDDM) without any ultrasound treatment even for high concentrations of the diamond material—up to 10% wt. and even higher. These colloid solutions are stable for many months and even years, and a very small amount (~1–3% of total diamond material weight) of the precipitate appears. The second group is much bigger and include all other investigated samples. These NDs cannot form a colloid solution without ultrasound treatment (NanoAmando, RUDDM non-fractionated, UDA-GO-SP-M1) or form only suspensions with micrometer-scale particle size even after an ultrasound treatment for 10 h. These suspensions are very unstable, and a precipitate begins to appear 5–10 min after the end of ultrasound exposure. The problem of the stability of ND solutions is crucial, but is far beyond the scope of this study. However, the suspension stability is an important aspect of ICP–AES.

Performing combustion procedures, we disclosed that different types of NDs required different temperatures for ashing. RUDDM and SDND required a lower temperature than other samples because at >600 °C it formed fused ash (Fig. 1, a leftmost crucible), which was almost impossible to remove from a crucible bottom. Combustion at 550–600 °C results in a loose, easily removable ash. However, RDDM burns noticeably only at high temperatures, at higher than 850 °C. Most of the samples turned to ash at around 650 °C in 2–3 h, but the combustion time should be determined experimentally

for each ND product name, because the formation of a fused ash slows down the combustion process significantly.

The next important stage is ash digestion. For this purpose, we used a mixture of HCl and HNO₃. According to the IR sensor, the process temperature inside digestion vessels was 180–220 °C depending on the ND product name. After the dilution, most of samples form colloid solutions without any precipitation. However, in several cases, we observed a loss of the amorphous precipitate after the dilution of mixtures. These precipitates consist of colloidal particles and drop down in 1–2 h. For some other samples (UDA-SP, UDA-GO-SP, UDA-GO-SP-M1, UDA-GO-SP-M2) ash digestion was incomplete, but undecomposed particles were small enough to be introduced through an ICP–AES nebulizer, and the amount of these particles was small compared to the initial amount of ash. Nevertheless, we tried to decompose such samples using another digestion mixture: HCl, HNO₃, and HF. We could not digest these particles totally, but these solutions were compared with those treated with HCl–HNO₃.

Preparation of acid extracts of impurities was the simplest. We use the term “extract” because almost all the initial ND material remains in its original form. For acid extraction, we used nitric acid as most widespread reagent for microwave-assisted digestion. In addition, we assumed that surface impurities are formed by the compounds that can be readily dissolved at 200 °C with nitric acid only. Temperature of process inside vessels, according to the IR sensor, was 180–220 °C depending on the ND product names. The data shows that the treatment of initial NDs with acids even at rather harsh conditions does not remove them completely. Nevertheless, some metals appeared in solution. However, it is the principle applicability of this approach that interested us, the selection of conditions for maximally complete removal of impurities without ND decomposition is a separate, very sophisticated task, which is out of the scope of this paper. Suspension of NDs readily coagulates in 2–3 h, then it is separated from the sediment and analysed.

3.2. ICP–AES analysis: preliminary studies

At the first stage of the ICP–AES analysis, we estimated the reproducibility of signal intensities for the same elements. This is a crucial moment for the estimation of the overall measurement quality, because the colloid solution immediately coagulates upon adding an internal standard solution, while suspensions precipitate with time. To do this, RUDDM 2012 and UDA-S-GO (10 mg/ml) were injected into the instrument 7 times along with the injection of an aqueous La solution (50 ppm). From these data, we calculated signal RSD



Fig. 1 – View of burnt at 700 °C NDs: fused ash (a leftmost crucible) and loose easily removed ash. From left to right: RUDDM 2012, RUDDM non-fractionated, UDA-S, UDA-S-GO; UDAG-S. (A color version of this figure can be viewed online.)

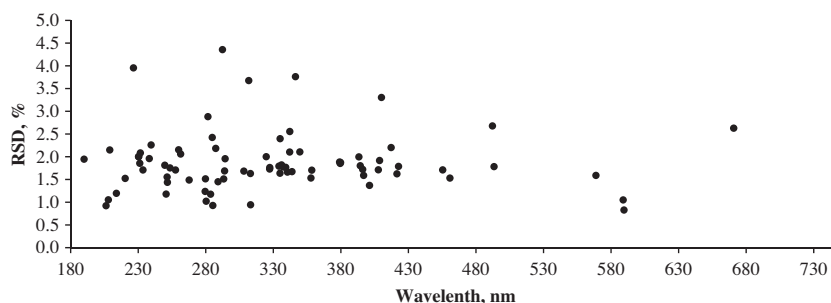


Fig. 2 – RSD for the AES signal of a RUDDM 2012 solution (10 mg/ml) at various wavelengths.

(Fig. 2). The figure shows that the RSD is at the level of 1–2% and no higher than 5%. No systematic change in intensity with time was observed, as the initial solution is very stable. For UDA-S-GO slurries, RSD was 3–5% and no higher than 7%; however, a small but significant signal decrease with time was observed for the third replicate, which can be accounted for by the suspension precipitation. Thus, in further experiments, we homogenized unstable slurries by shaking them right prior to the experiment.

At the next stage, we made a semiquantitative analysis of all the initial nanodiamonds. As a result, we estimated the levels of concentrations of various elements in samples and prepared the most suitable calibration sets for quantification. This semiquantitative analysis was made for colloid solutions and slurries (with ND concentrations of 10 mg/ml) to minimize the possibility of pollution.

We also found out that some lines could not be used for quantification as they show strong spectral interferences with other elements. For instance, 281.615 nm line was only suitable for Mo and 220.353 nm for Pb. Samples with high concentrations of Ag show the overestimation of W at 224.876 nm. All these features, as well as correct boundaries for calibrations (with due regard to line intensities) were taken into account while building the worksheet of the spectrometer data-gathering software. As a whole, it allowed us to reliably conclude that our qualitative analysis is free from errors due to spectral interferences. As a result, we found out about 20 major elements and a considerable variation of their concentrations throughout the samples. Moreover, we found that some samples have some uncommon elements like Ag, Ce, Y, Hf, Zr, and Hg, which are discussed in more detail in the next section. In such a case, both semiquantitative analysis and quantification was made using several lines. All these elements were found by their most intense lines and only for several ND types. All the elements were found in slurries and then confirmed in the analysis of digested samples and extracts.

To correct the concentrations, we measured sample moisture. The data is presented in Table 5. It shows that the moisture of almost all the samples is in range 2–5%. After moisture measurements, several samples were left in air and re-measured after 1 h. As a result, we obtained the same moisture values. Beside this, we observed that sample weight started increasing immediately after heating is finished. Therefore, we assumed that it is physically absorbed water vapor from the surrounding air and 2–5% of moisture corresponds to the equilibrium water content at ambient conditions. Thus,

Table 5 – Moisture content in nanodiamond samples ($n = 3$, $P = 0.95$).

NDs product name	Moisture content, wt.%
RDDM	1.3 ± 0.1
RUDDM 2011	4.9 ± 0.2
RUDDM 2012	5.6 ± 0.2
RUDDM non-fractionated	5.0 ± 0.2
SDND ^a	4.6 ± 0.2
G ^a	5.0 ± 0.2
NanoAmando	3.0 ± 0.1
DNA-TAN	2.9 ± 0.1
DNA-STP	3.0 ± 0.1
UDAG-S	2.2 ± 0.1
UDA-S	4.9 ± 0.2
UDA-S-GO	5.0 ± 0.2
UDA-SP	2.8 ± 0.1
UDA-GO-SP	4.3 ± 0.2
UDA-GO-SP-M1	3.6 ± 0.1
UDA-GO-SP-M2	3.5 ± 0.2
UDD-NanoGroup	6.6 ± 0.2
UDD-Alit	2.3 ± 0.2

^a Samples after drying and keeping in air during several days.

we can state that absolutely dry samples and samples with moisture above 2–5% under such conditions are unstable. Consequently, if it is necessary to prepare NDs solutions with the maximum precise weight concentration or to determine impurities with the maximum accuracy, water content should be measured and taken into account.

3.3. Quantitative ICP–AES analysis

Finally, all the prepared solutions, including slurries, acid extracts, and digested ash were analysed under the same conditions. Fig. 3 shows the results of the comparison of element concentrations calculated from the data for all the three types of sample preparation (for brevity's sake, only the data for four elements are shown).

They show that, as a whole, all the three approaches correlate well, although some elements stand out from this dependence. For instance, Zr dissolves only partially, while Ti, W, Cr, and Sn almost do not go into the solution under nitric-acid treatment (this result was constantly observed for all the samples with the concentrations of these elements >50 ppm), neither for 1 h, nor for 3 h. This is probably due to non-optimum conditions of dissolution of these elements.

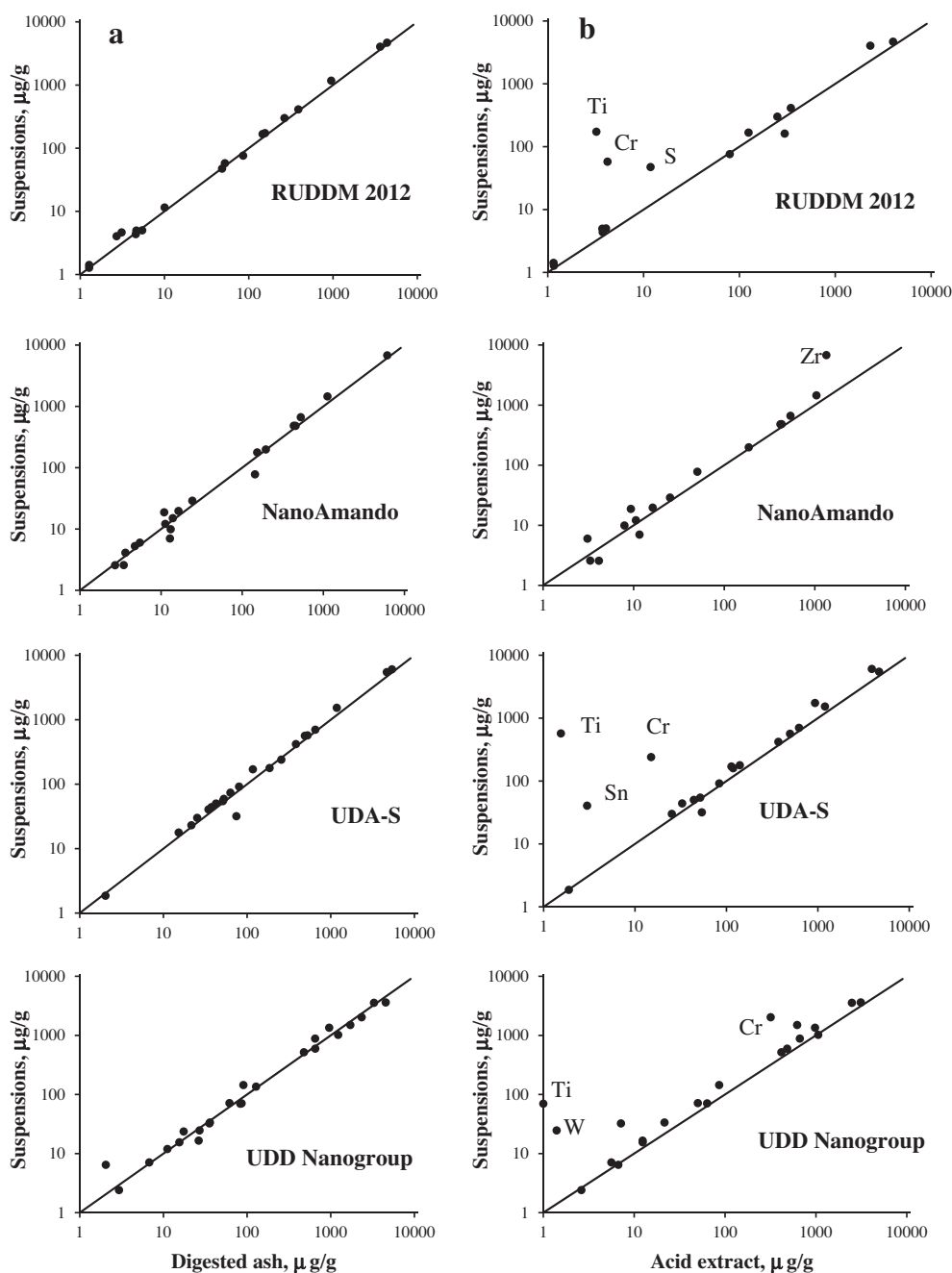


Fig. 3 – Correlations between the concentrations obtained by the results of analysis of (a) slurries and ashing and (b) slurries and acidic extraction. The lines correspond to $r = 1$.

To the contrary, the treatment with HNO_3 for 3 h at 200 °C is rather harsh conditions, and, probably these elements are not only at the surface, but also in the crystallite nuclei; or at the surface as difficultly soluble compounds (oxides or carbides). Some researchers claim that it is not possible to remove impurities from NDs as they form the crystal itself [10]. We cannot say that our data prove this hypothesis but guess that this problem is worth a separate detailed study, which was out of the scope of this paper.

Moreover, as we further proved, for an uncommonly high concentration of an element, we see the memory effect of Teflon vessels, which results in an overestimated concentra-

tion in the next sample; thus, this required cleansing the vessels with nitric acid for 20 min under all other oven parameters left unchanged. For eight samples, we made acid extraction for 1 and 3 h. The comparison showed that the extraction efficiency for 3 h is much higher than that for 1 h, but still is not enough for 100% recovery of elements.

Thus, we proved that the results for slurry analysis are reliable and adequate. As the contamination of samples is minimum in this case, to calculate the amount of impurities in the initial ND powders we selected the data of the direct analysis. Results of dispersion analysis are presented in Table 6. The results are grouped in concordance with the

Table 6 – Elements contents in nanodiamonds samples, determined directly in dispersions (all concentrations are in ppm, results uncertainty is $\pm 15\%$).

El.	1 ^a	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Ag	–	–	–	–	660	–	800	370	–	–	–	–	–	–	–	–	–	–	–	–	–
Al	4	300	300	425	530	265	10,500	370	835	700	23	15	18	701	700	310	44	84	30	1020	85
B	305	–	1170	–	535	–	80	–	–	–	35	–	–	–	–	–	–	–	320	140	–
Ba	–	–	–	–	25	–	22	–	–	4	–	12	–	23	3	11	3	2	–	7	1
Bi	–	–	–	–	3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Ca	–	78	76	1000	280	15	300	16	16	12	135	41	14	5470	720	57	65	680	24	3550	340
Cd	–	–	–	–	–	–	3	2	–	–	–	–	12	–	–	–	–	–	–	–	–
Ce	–	–	–	–	7	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Co	–	1	1	2	2	–	–	–	–	–	2	2	–	2	–	–	–	–	–	2	–
Cr	15	57	58	20	11	7	150	8	13	7	290	160	8	240	70	1630	520	700	280	2030	320
Cu	33	410	410	855	20	50	120	30	75	4	42	33	13,100	420	180	50	30	100	40	70	6
Fe	133	4100	4040	5680	1780	780	2680	400	1380	564	1820	1200	5730	6050	2450	7940	1080	4100	4250	3600	730
Hf	–	–	–	–	–	–	–	–	–	40	–	–	–	–	–	–	–	–	–	–	–
Hg	–	–	–	–	–	–	–	–	–	–	–	–	900	160	80	–	–	–	–	–	–
K	–	–	–	4	20	23	42	–	–	–	85	9	230	45	34	14	18	110	9	145	14
Mg	–	8	–	30	40	–	30	–	5	–	15	–	9	563	56	8	9	100	–	517	31
Mn	–	5	5	23	21	43	18	2	15	6	4	2	30	54	9	6	6	13	5	71	5
Mo	4	12	11	11	13	4	24	5	10	7	70	101	–	60	50	83	36	43	20	32	37
Na	8	4660	4680	60	10,800	3	25	7	14	41	130	27	2	180	30	14	19	100	5	880	1200
Ni	86	170	170	190	15	2	34	–	6	9	35	17	7	32	11	46	34	60	8	600	21
P	–	–	–	27	11	21	100	–	–	–	91	27	160	170	74	5100	–	80	2660	33	10,700
Pb	52	55	55	33	5	20	30	26	4	–	6	6	145	90	100	13	16	12	30	6	5
S	24	80	47	40	38	201	15	–	–	180	430	280	103	1530	700	380	330	1200	285	1350	140
Sb	–	–	–	–	10	3	6	–	–	–	5	3	–	74	60	5	4	3	–	–	3
Si	180	170	160	620	1470	1250	1260	200	343	300	210	425	500	1740	2280	810	150	1720	255	1500	100
Sn	–	4	4	5	170	32	175	–	45	–	9	8	4	40	17	25	13	15	20	24	3
Sr	–	–	1	7	5	–	3	–	–	–	–	–	–	50	4	–	–	–	–	15	3
Ti	51	174	173	165	285	34	170	86	230	14	1300	1460	12	570	520	540	470	340	400	70	410
V	–	–	–	–	–	–	7	–	10	–	–	–	–	7	6	7	–	3	–	75	5
W	11	4	4	3	60	15	63	31	30	85	130	21	21	18	12	63	10	13	3	25	5
Y	–	–	–	–	–	–	–	–	–	200	–	–	–	–	–	–	–	–	–	–	–
Zn	4	8	4	20	3	2	90	2	5	4	13	20	2400	30	20	25	6	25	32	17	22
Zr	23	4	5	5	17	–	25	4	2	3200	4	5	–	3	2	3	5	3	2	12	13
Σ	933	10,270	11,380	9210	16,840	2760	16,750	1560	3030	5350	4870	3860	23,400	18,300	8180	17,100	2860	9500	8680	15,800	14,200

– Means <1 ppm.

Content of non-presented elements: Cs and Rb < 100 ppm; As, Ge, Se, and Tl < 10 ppm; Au, As, Be, Dy, Er, Eu, Ga, Gd, Ge, Ho, In, Ir, Li, Lu, Nb, Nd, Os, Pd, Pr, Pt, Re, Rh, Ru, Sc, Sm, Ta, Tb, Ta, Th, Tm, U and Yb < 1 ppm.

^a 1 – RDDM; 2 – RUDDM 2011; 3 – RUDDM 2012; 4 – RUDDM non-fractionated; 5 – SDND; 6 – G; 7 – G01; 8 – G02; 9 – G01P; 10 – NanoAmando; 11 – DNA-TAN; 12 – DNA-STP; 13 – UDAG-S; 14 – UDA-S; 15 – UDA-S-GO; 16 – UDA-SP; 17 – UDA-GO-SP; 18 – UDA-GO-SP-M1; 19 – UDA-GO-SP-M2; 20 – UDD-Nanogroup; 21 – UDD-Alit.

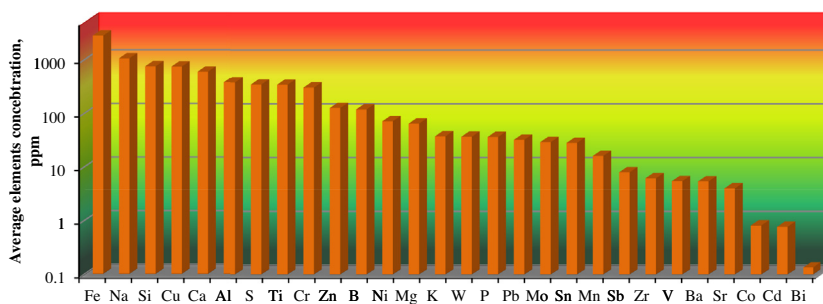


Fig. 4 – Average common elements content in tested NDs samples. (A color version of this figure can be viewed online.)

manufacturer list in Table 1 for comparison's sake. Considering weighting, dissolution, and calibration uncertainty, we estimate the total uncertainty as 15%. Here we give all values for air-dry NDs. Fig. 4 shows mean values of elemental composition. Some values standing out of the picture (e.g. three samples with very high concentrations of phosphorus) were excluded from the calculation to avoid distorting the general picture. Uncommon elements, which are found in certain samples only (Ag, Hg, Y, Ce, and Hf), see below for details, were excluded as well.

This total analysis unravels some interesting regularities. All the elements can be divided by their mean concentration into several groups. First, the most obvious is that the major metal impurity in all the samples with no exclusions is iron. Its concentration is usually hundreds and thousands ppm, which is well expected as the detonation synthesis is performed in steel chambers. Close to iron is a group of elements with mean concentrations of 100–1000 ppm. These are components of the steel of the detonation chamber or explosion initiators (Ti, Cr, and Cu). In addition, the elements existing in natural waters (Na, Si, Ca, Al, and S) in high concentrations manifest themselves here as well. The third group (<100 ppm) consists of all other elements; their sources can be either the materials of technology lines and vessels or the impurities in the used reagents and water. As a whole, the concentrations of impurity elements cover a very wide range both for a single sample and in samples from different manufacturers.

The reliability of metal determination shows that ICP-OES is a suitable tool for studying complex NDs biotoxicity. For example, such elements as Cu, Fe, Zn, Ti, etc. should be taken into account [14,16–18,29], and thus, such amounts of these elements in NDs can be significant for biomedical research and samples involved in this research require some pretreatment and purification. As well, the amounts of Ni, Fe and some other elements (Table 6) are at the level where its catalytic activity is significant [30–33] and, thus, should be taken into account in such studies. This clearly proves that the monitoring of the purity of nanodiamonds for high-technology and medical applications is undoubtedly necessary. RUDDM and NanoAmando samples produced at different dates show that even NDs of the same manufacturer retain the qualitative composition, while the quantitative composition changes. RUDDM samples produced at different dates show that even NDs of the same manufacturer retain the qualitative composition, while the quantitative composition changes.

3.4. Uncommon elements

As we mentioned above, semiquantitative analysis of some samples showed the emission at lines corresponding to relatively uncommon elements. Thus, at the stage of quantification, we paid special attention to these elements. This was dictated by the fact that one of the crucial drawbacks of ICP-AES is the existence of spectral interferences, which distort (and commonly increase) the signal of the test element under the quantification or provide a false positive signal under qualitative analysis.

In particular, SDND, G01, and G02 samples (all from the same manufacturer) show silver (400–700 ppm) at lines of 328.068 and 338.289 nm, which do not interfere with the lines of other elements found in these samples. In addition, SDND shows trace cerium (7 ppm). For the determination of cerium, we used lines of 418.659, 446.021, 456.236, and 462.816 nm. The latter sits at the shoulder of the argon line of 462.844 nm and, thus, was excluded from the final calculation. Only for SDND samples, we found small signals in all the lines giving similar concentration values. Probably, these elements are components of the know-how catalyst used by the manufacturer during intense acid treatment [51], or of the catalyst of the ND detonation synthesis itself.

In NanoAmando, we found relatively high concentration of zirconium (at 327.307, 339.198, 343.823, 349.619 nm), 0.3% wt., as its manufacturing involves wet grinding of the initial NDs in a ball grinding mill using yttrium-stabilized zirconia beads for several hours [52]. The amount of zirconium was so large that we succeeded in reliably determined hafnium (at 263.872, 277.336, 301.290, 339.979 nm), which always accompanies zirconium. The amount of Hf is 40 ppm. In other samples, only trace zirconium was detected.

Moreover, NanoAmando sample show mediocre (200 ppm) amount of yttrium (360.074, 371.029, 377.433, 437.494 nm), and all the four lines show very similar concentrational results, which are not warped by any interferences from other elements. Other samples show no emission at these wavelengths. The source of yttrium is probably the same grinding balls.

Mercury was determined at two wavelengths of 194.164 and 253.652 nm. It should be mentioned that the sensitivity of ICP-AES for mercury without a hydride-generation unit is low, with the determination limit of 50 ppb in liquids, which means 5 ppm in powder samples. Nevertheless, three slurry samples (see Table 7) showed distinct signals at both lines; the same signal were obtained from acidic extracts. In fact,

Table 7 – Comparison of mercury contents in nanodiamond samples determined with flameless pyrolysis atomic absorption spectroscopy (FPAAS) and ICP-AES.

NDs product name	Moisture content, wt. %	Mercury content in air-dry samples, ppm		
		FPAAS	ICP-AES	
			Acid extract	Slurry
UDA-S-GO	5.0 ± 0.2	42 ± 2	50 ± 8	77 ± 11
UDA-S	4.9 ± 0.2	126 ± 15	118 ± 20	160 ± 24
UDAG-S	2.2 ± 0.1	717 ± 30	790 ± 120	800 ± 140

we have already found significant amounts of mercury in some NDs using flameless pyrolysis atomic absorption spectroscopy [53]. This method is very widespread for mercury determination in various materials, has a very high sensitivity and absolute selectivity guaranteed by a hollow-cathode lamp. The ICP-AES results are in good concordance with AAS analysis (Table 7). As for the possible cause of such strong contamination of ND samples with mercury, it could result from the washing of NDs during their production using a water source with a high mercury concentration.

3.5. Summary

These approaches can be used not only for ND samples, but also for other nanomaterials and depending on the specific aims of the task. Each of them has their own advantages and drawbacks. Ashing analysis with subsequent ash digestion is the most classical approach providing complete exclusion of matrix effects. In fact, it is most versatile from the viewpoint of the sample type and, under correct selection of ashing and dissolving conditions, provides most reliably determined total amounts of heavy metal impurities. However, it has significant drawbacks: long and laborious sample preparation, complete sample decomposition, complete loss of volatile elements (Hg, As, S, etc.), and a partial loss of moderately volatile elements (Zn, Pb, etc.) at the ashing stage. Besides, the ash from some samples can be very difficult for digestion, especially if the combustion takes place at high temperatures and the formation of carbides and silicides is possible. In the case of ICP-based measurements and low amounts of resulting undissolved particles, this problem is mainly not crucial as these particles appear in the plasma.

The best feature of acid extraction is that it provides the analysis without sample decomposition and, in fact, is a purification method. In our opinion, it is the most convenient method for the ND manufacturing as the sampling can be at line of the purification flow; thus ensuring the process monitoring. As in the case of complete digestion, it is not affected by the carbon matrix, and sampling is much more rapid and simple; and no loss of volatile elements is exhibited. Unfortunately, this method provides the determination of only the impurities that are located at the surface and are dissolved in acids. Moreover, it requires the selection of conditions for dissolving certain nanodiamonds and impurities to be determined.

Direct analysis of nanodiamonds demands the minimal sample preparation: ultrasonic-assisted dispersing and even

no sonication may be required for some samples. This leads to the least probable contamination of the test samples and the most reliable analysis results. This method is indifferent on the impurity location (at the surface or within the crystals); chemically inert species of impurity elements are also taken into account (like heavy metal carbides). Labile substances are not lost as well. In principle, it is possible to determine the amount of carbon in NDs by ICP-AES directly, but this problem requires some further studies. The drawbacks of direct slurry nebulization are irreversible consumption of a part of sample reaching the plasma and very strict requirement of the use of the internal standard for the quantification. In addition, the analysis of NDs that does not form stable colloid solutions are relatively stable suspensions with submicrometer particle size seems difficult. A part of the slurry condensed at the spray chamber of the ICP-AES instrument can be gathered and reused, although it will be contaminated with the internal standard. In this research, we used a high-sensitive concentric nebulizer, but Noordermeer V-groove or Modified Lichte nebulizer should be recommended for routine analysis. They have a lower sensitivity, but a very high clogging resistance.

4. Conclusions

Thus, we developed a procedure for quantitative multielement analysis of ND impurities by ICP-AES using a slurry nebulization technique, ashing and digestion, and acid extraction. We found out that the most of the tested NDs contain relatively high amounts of Fe, Na, Ca, Si, Cu, Al, S, and Ti (>100 ppm), while Pb, Zn, K, Mn, B, Cr, Mg, Mo, Sn, W, Ba, Sb, Co, and Sr are in low but significant amounts. In addition, we found some uncommon elements like Ag, Ce, Y, Hf, Zr, and Hg in several samples. This means that the purification process is possible, but its current variant needs improvement. We have found that NDs from different manufacturers contain very different impurities and, even for a single product type, they change from lot to lot. This means that ND purity needs to be monitored, and additional purification might be made, if necessary. In our opinion, the introduction of the instrumental monitoring of the purity of produced nanodiamonds may facilitate advancing their production technology. The proposed method of ICP-AES analysis uses commercial instruments and reagents, is relatively simple for industrial applications, and is widely used in practical analyses for determining the elemental composition both in research and plant laboratories. It should be noted that after

software worksheet preparation and the optimization of ICP–AES parameters for specific instrument, the analysis might be performed as routine. Thus, we believe it can be used as a basis of the development of the instrumental monitoring practice for nanodiamonds.

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